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## NANOPOROUS CERAMICS BASED ON ORGANOSILICON POLYMERS

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Using the BET, IR, and mass-spectrometry methods, the effect of pre-pyrolysis heat treatment in nitrogen and in air on the structure of nonporous ceramics obtained by pyrolysis of an organosilicon polymer in nitrogen at a temperature of 600°C is investigated. An explanation of the effect of pre-pyrolysis heat treatment and its conditions on the formation of the structure of the polymer and the polymer-based ceramic is offered in the context of synergism.

Ceramics with nanopores is continuously finding wider areas of application in separation processes, as molecular sieves in chemical processes, as filters for gas purification at high temperature, sensors, and in other fields. Ceramic ultrafiltration membranes consist of a substrate with sufficiently large pores (the pore diameter 1 – 15  $\mu\text{m}$ ), an intermediate layer (pores of size 100 – 150 nm), and a working layer (the pore size less than 1 nm). Membranes with pores ranging from  $10^{-10}$  to  $10^{-9}$  m uniformly distributed in the material can be obtained by the pyrolysis of polymers [1].

The structure of ceramic materials is formed as a consequence of complicated irreversible and nonequilibrium physicochemical processes. For their understanding it is convenient to apply the main principles of the physics of open systems, thermodynamics of irreversible processes, and synergism. According to the contemporary concepts, all natural processes are irreversible and nonequilibrium [2]. Systems that are regarded as a segments of space separated by a real or imaginary boundary from the surrounding space evolve in the stability – instability – stability sequence, or, in other words, an attractor – a bifurcation – an attractor sequence [2]. The entropy of a system may not only increase, but decrease as well, i.e., self-organization is observed. Synergism considers the processes of self-organization, stability, and disintegration of structures in systems [2].

Real systems are combinations of order and chaos and they are described using the geometry of fractals [2]. The processes in open systems are determined by the degree of nonequilibrium, i.e., the intensity of their material exchange with the ambient medium. When a system is in a stable state, a negative feedback functions in it. According to the Le Chatelier – Brown principle, the system creates structures impeding an external influence. When a system is in an unsta-

ble state, a positive feedback is observed and the system acquires increased sensitivity to internal fluctuations and external disturbances. An unstable state may be a bifurcation. A bifurcation is a manifestation of the probabilistic aspect of matter.

The unstable and multistable states (multistabilities) in a system have a determining effect on the evolution of the material structure in various stages of ceramic technology [3]. The presence of a multistability with stable states perceptibly different in their properties, into which states the system may fall after passing an unstable state, leads to poor reproducibility of the structure and properties of ceramics [4].

An effective way of improving the reproducibility of a ceramic structure is influencing the system in the range of the main unstable state for the purpose of eliminating the multistability. If the unstable state is a bifurcation, one can talk of eliminating the bifurcation instead of eliminating the multistability [3]. The enhanced sensitivity of a system in an unstable state to weak effects allows a technologist to influence the evolution of a ceramic structure. In this case the controlling effect exerted on the system exceeds the noise level, i.e. the level of small inner and outer uncontrollable effects. This makes a further evolution of the system more predictable and allows for better reproducibility of the structure and properties of obtained ceramic materials. [3]. The controlling effects may be internal, i.e., existing inside the system, or external, i.e., acting from outside. If the multistability in a system with stable states highly different in their properties is removed due to internal effects, this is equivalent to a manifestation of the prehistory of the system, since these effects were built in the system in the previous stages of the technological process. The role of internal effects in ceramic materials is usually played by the structural elements [3].

The purpose of this study was to investigate the effect of pre-pyrolysis treatment on the modification of the structure of ceramics, primarily the pore structure in the course of py-

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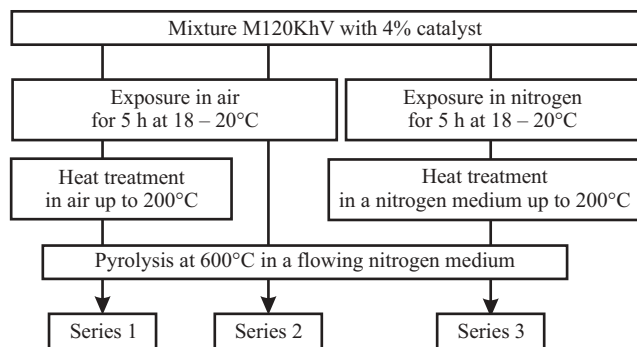


Fig. 1. Scheme of sample preparation.

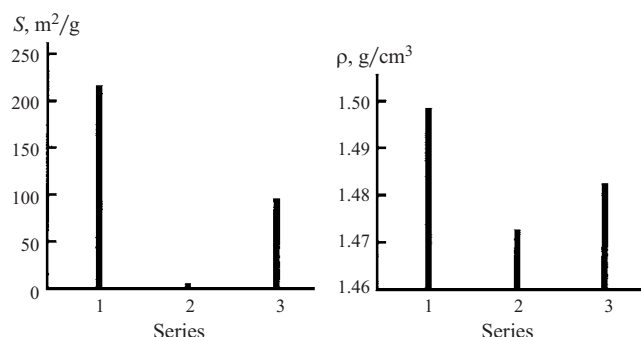


Fig. 2. Specific surface area  $S$  and density  $\rho$  of samples.

pyrolysis. The pore-formation processes in the course of pre-pyrolysis treatment and subsequent pyrolysis are discussed in the context of synergism.

The production of porous ceramics from precursor polymers usually includes the following stages [5]:

- synthesis of thermoreactant polymers from monocompounds or oligomers with a controlled molar weight distribution;
- molding an intermediate article (casting, extrusion, compression, fiber drawing, etc.) and subsequent heat treatment at 150 – 250°C to form a solid thermoreactant polymer;
- pyrolysis in an inert atmosphere or in an atmosphere reacting with the polymer at 500 – 1500°C, including the removal of organic inclusions within a temperature interval of 400 – 800°C and formation of an amorphous inorganic material that crystallizes at temperatures of 1000 – 1600°C.

To obtain a ceramic material with open nanopores, the most essential is the range of pyrolysis in the interval of 550 – 750°C [6]. At these temperatures the emission of gases is the most intense, and cracks may arise up to a fracture of the sample. In the course of removal of gases formed under pyrolysis, the polymer structure transforms into a ceramic structure. This is accompanied by a modification of the gas removal mechanism and the deformation characteristics of the material. To remove the released gases, the system, by way of self-organization, forms a network of channels facilitating the exit of gases from the material. Polycondensation (cross-linking of the polymer chains) is accompanied by re-

lease of heat and water, whose molecules acquire sufficient energy to pass through the material. An additional input of heat is implemented in heating under pre-pyrolysis treatment. The gases exit via the least dense areas of the molded article, which arise in polycondensation and subsequent heating.

The condensation of the material occurring when the polymer transforms into a ceramic results in the fact that the emerging gases are emitted by diffusion [6]. It should be taken into account that the deformation properties as well change from elastoplastic (in the polymer) to brittle (in the ceramics). If gas emission is too intense for its diffusion via the solid phase, the system (the sample) forms a network of nanochannels allowing the pyrolytic gasses to exit from the material. In subsequent heating (to 800 – 900°C), cylindrical nanochannels may transform into a series of sufficiently large nanopores, which reduces the surface area and lets the system decrease its free energy. However, the effect of pre-pyrolysis treatment on the properties of the obtained material is not yet clear.

In the production of a nanoporous ceramic material we used a methylsiloxane polymer with the trade name SR350 in the form of a ready 43 – 45% solution in a mixture of xylene isomers (Basilone Harz M 120 XB, GE Bayer Silicones GmbH). The catalyst for cross-linking of polymer chains was 3.2 aminoethylamine. Three series of samples were prepared in accordance with the following scheme (Fig. 1).

Samples mixed with the catalyst were exposed at room temperature in the form of a thin (2 – 3 mm) layer in a Petri dish. The exposure and pre-pyrolysis heat treatment was performed in air for samples of series 1 and 2, and in nitrogen for series 3. The heat treatment program included an increase in the temperature from 20 to 200°C at a rate of 60 K/h, and three 2-h exposures at 80, 140, and 200°C, after which the temperature was lowered to 20°C also at a rate of 60 K/h. In pyrolysis, the temperature was increased at a rate of 120 K/h to 500°C, then raised to the final temperature of 600°C at a rate of 30 K/h, exposed at the final temperature for 4 h, and cooled (120 K/h).

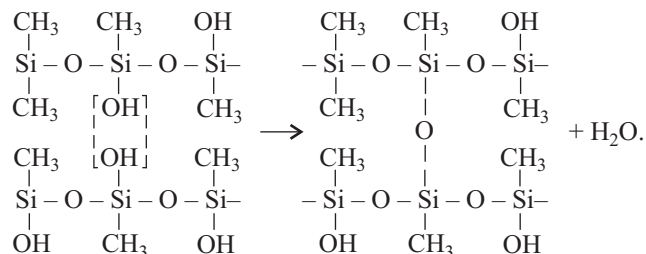
The real density of the obtained samples was measured using the gel-pycnometry method (Micrometrics, AccuPyc 1330). The specific surface area was measured by the BET gas-absorption method (Micrometrics, Gemini). The structure of the material was studied using infrared spectrometry (a BIO-RAD FTS-60A spectrometer). The gases released in heating were analyzed using a mass-spectrograph (Omnistar, Balzer Instrument).

Differences in the samples could be observed at a glance. The air-dried sample is more brittle than the sample dried in nitrogen. The samples pyrolyzed without preliminary drying have a light brown color and are transparent, and the samples subjected to drying, on the contrary, are quite opaque.

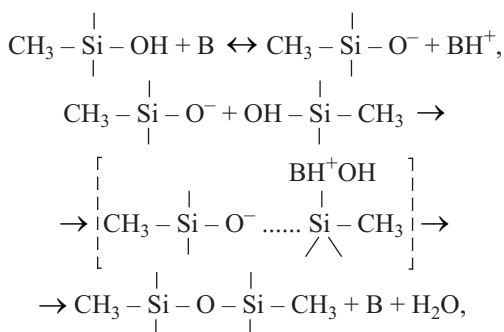
A strong dependence of the specific surface area on the existence and conditions of pre-pyrolysis heat treatment was identified (Fig. 2).

The mass-spectroscopy results of the emitting gasses indicated the following.

Water release is most intense at temperatures from 20 to 200°C, continues up to 300°C, and is a result of polycondensation reactions (cross-linking of chains)



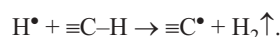
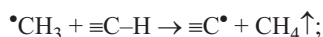
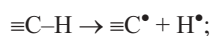
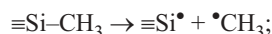
The methylsiloxane chains are cross-linked in heating up to 90°C. The reaction can proceed at room temperature as well when adding sufficiently strong organic bases which contain amino groups ( $-\text{NH}_2$ ) or ammonia groups ( $\text{NH}_4$ ), for instance: *p*-aminotrimethoxysilane,  $\gamma$ -aminopropyltriethoxysilane, and acetylmethylammonium bromide [7]:



where B is the base.

The volatilization of the solvent continues up to 300°C but is the most intense at temperatures of 80–200°C.

Rather intense peaks of methane are observed already at the room temperature, possible as a result of methyl groups breaking off from the silicon atoms. The occurrence of this reaction at such a low temperatures is presumably accounted for by the possibility of concentration of energy, which is released in the exothermic polycondensation reaction, on these bonds. The most intense emission of methane and hydrogen is observed at temperatures over 500°C, which agrees well with the following reactions:



Cyclic or linear fragments of polymer molecules are present (in trace quantities) nearly in all stages of heat treat-

ment, but are clearly expressed at a temperature of 160–200°C. This agrees with the literature data (U.S. Patent No. 2913471).

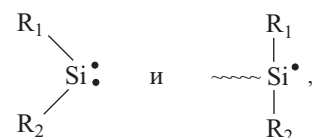
The study of the IR spectra made it possible to make the following conclusions.

After pyrolysis at a temperature of 600°C, free OH groups are virtually absent from the material.

If the material has been pyrolyzed without pre-pyrolysis heat treatment, it contains a greater amount of residual  $-\text{CH}_3$  groups. This corroborates the fact that methyl groups start breaking off at low temperatures. In the course of pre-pyrolysis heat treatment, methyl groups are already removed from the material, and after pyrolysis they decrease,

As a result of pre-pyrolysis heat treatment, the number of  $-\text{Si}-\text{O}-\text{Si}-$  bridges decreases and single bonds  $-\text{C}\equiv\text{C}-$  and  $-\text{C}=\text{C}-$  arise, i.e., the transformation of the organic structure into an inorganic one is delayed. This is evidence of a decreased degree of nonequilibrium of the transformation process. Such conditions develop prerequisites for a controlling effect on the evolution of the structure of internal controlling signals, i.e., the structural elements created in the preceding technological stages. In our case this is the inheritance of the polymeric structure formed in the course of pre-pyrolysis treatment.

The presence of  $-\text{Si}=\text{CH}_2$  bonds in the intermediate product and the presence of  $-\text{Si}-\text{O}-\text{C}-$  branches in all samples subjected to pre-pyrolysis treatment in air testifies to the radical mechanism of the oxidizing reactions. In this case the formation of free radicals with the following structure is possible:



where  $\text{R}_1$ ,  $\text{R}_2$  are  $-\text{OH}$ ,  $-\text{H}$ , and  $-\text{CH}_3$  groups;  $\sim\sim\sim\sim$  is a polymeric chain,

the above radicals enter in reactions and form a double silicon-carbon bond and the structure  $\equiv\text{Si}-\text{O}-\text{CH}_3$  [8].

The obtained experimental results can be accounted for in the context of synergism.

When a polymer is mixed with a catalyst, cross-linking of the polymer chains and formation of the  $-\text{Si}-\text{O}-\text{Si}-$  skeleton starts (the polycondensation reaction). In spite of thorough mixing of the catalyst with the polymer, these reactions proceed nonuniformly inside the volume of the material, and as a result, a leather-like substance with heterogeneous microlevel densities is formed after 5 h of exposure. In certain areas the density is higher, and in other areas, where the polycondensation was slower or the polymer chains had a different layout, the density is lower. When a cross-linked polymer layer is sight-checked, such heterogeneous densities appear as sites with different (higher or lower) transparency.

A system under heat treatment forms channels of open pores for gas emission. The channels divide the system into

fragments (blocks), whose size depends on the degree of nonequilibrium of the process [3] (the higher the degree of nonequilibrium, the smaller the size of the fragment [2]). Nanopores with a narrow size distribution arise on the site of evaporating organic components of the organosilicon polymer, while its residual structure is preserved.

If the leather-like material is immediately subjected to pyrolysis, the following may occur. The intense gas emission and the high degree of nonequilibrium of the process will increase the size of the channels, develop compressive stresses in emerging fragments, and lead to the disintegration of the structure into smaller fragments. Inside these fragments, most probably due to the mechanical compressive stresses, there will be developed the conditions for the elimination of nanopores and their merging with larger channels and pores. The internal energy of the system will diminish due to the formation of an infinite cluster consisting of sufficiently large open pores. A decrease in the quantity of the nanopores and their transformation into larger pores will result in the smallest total specific surface area (Fig. 2). At the same time, the shrinkage of the samples will be the lowest among the considered three series of samples, which will decrease the apparent density of the ceramics.

The emission of different gases (solvent, water vapor, methane, etc.) in the course of pre-pyrolysis heat treatment proceeded slowly and under low temperatures. A smooth increase in the temperature and the exposures at 80, 140, and 200°C contributed to the fact that the gas release occurred mainly in the less dense sites. As a result, a further decrease in the density continued in the less dense sites and an increase in density continued in the denser sites, i.e., the prerequisites for the formation of channels without open pores were created under a rather low degree of process equilibrium; consequently, the channels had a relatively small diameter compared with the case described above, and the blocks were larger. Such a structure formed in the stage of pre-pyrolysis treatment and consisting of relatively large blocks separated by less dense sites, in subsequent pyrolysis prevented the coalescence of nanopores in the system and facilitated their conservation. It should be noted that after pre-pyrolysis treatment the samples did not yet have open pores.

The largest specific surface area of the pores could be obtained after pre-pyrolysis thermal treatment in air (Fig. 2).

Oxidation facilitated the gas emission and the formation of a structure of a heterogeneous density, possibly because oxygen primarily attacked the sites with a lower density, initiating free-radical reactions and cutting the polymer chains.

The conditions of pre-pyrolysis heat treatment have a determining role in the evolution of a ceramic structure during the subsequent pyrolysis and provide for the formation of a great number of nanopores and their narrow size distribution. A decrease in the degree of nonequilibrium of the process in unstable states, in particular, in gas emission, leads to the formation of an optimum structure of open-pore channels and the material fragments formed by these channels, which helps to preserve the nanopores with a narrow size distribution and provides for a large specific surface area of the pores. Further studies in this field will enable one to better control the properties of obtained nonporous ceramic materials. Special attention in this case has to be paid to identifying the ranges of unstable states with multistability and eliminating the multistability exercising external or internal effects (exceeding the noise level) on the system.

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